



## Formulation of zein coatings for apples (*Malus domestica* Borkh)<sup>1</sup>

Jinhe Bai<sup>a</sup>, Victorine Alleyne<sup>b</sup>, Robert D. Hagenmaier<sup>c</sup>, James P. Mattheis<sup>d</sup>,  
Elizabeth A. Baldwin<sup>c,\*</sup>

<sup>a</sup> Department of Horticultural Sciences, University of Florida, Gainesville, FL 32611, USA

<sup>b</sup> Florida Department of Citrus, Citrus Research and Education Center, Lake Alfred, FL 33850, USA

<sup>c</sup> Citrus and Subtropical Products Laboratory, US Department of Agriculture, Agricultural Research Service, 600 Ave. S.N.W.,  
Winter Haven, FL 33881, USA

<sup>d</sup> Tree Fruit Research Laboratory, US Department of Agriculture, Agricultural Research Service, Wenatchee, WA 98801, USA

Received 20 February 2002; accepted 30 August 2002

### Abstract

High gloss coatings are used to improve apple fruit (*Malus domestica*, Borkh) appearance and sales. The industry standard has been shellac-based formulations, which have problems with whitening, low gas permeability, and association with non-food uses. Zein, a natural corn protein, was used to formulate alternative, shiny coatings by dissolving zein in aqueous alcohol with propylene glycol (PG). Gloss levels on ‘Gala’ apple surfaces varied due to zein and PG content in coating formulations from that of controls to levels observed for shellac-coated fruit. At least 4% (by weight) PG was necessary for adequate gloss. However, increasing levels of both compounds resulted in increased gloss. Whitening, which occurred on the coated fruit surface upon wetting, was reduced by decreasing zein content to less than 11%. Permeability to CO<sub>2</sub>, O<sub>2</sub>, and water vapor was strongly dependent on the zein content in the coating. Internal CO<sub>2</sub> and O<sub>2</sub> in zein-coated ‘Gala’ fruit ranged 4–11 and 19–6 kPa, respectively, by increasing zein content in the coatings. An optimum formulation with 10% zein and 10% PG was developed, applied to ‘Gala’ apple, and was found to maintain overall fruit quality comparable to a commercial shellac coating.

© 2002 Published by Elsevier Science B.V.

**Keywords:** Gloss; Whitening; Permeance; Modified internal atmosphere; Volatile; Sensory

\* Corresponding author. Tel.: +1-863-293-4133x120; fax: +1-863-299-8678.

E-mail address: [ebaldwin@citrus.usda.gov](mailto:ebaldwin@citrus.usda.gov) (E.A. Baldwin).

<sup>1</sup> Mention of a trademark or proprietary product is for identification only and does not imply a guarantee or warranty of the product by the US Department of Agriculture. The US Department of Agriculture prohibits discrimination in all its programs and activities on the basis of race, color, national origin, gender, religion, age, disability, political beliefs, sexual orientation, and marital or family status.

## 1. Introduction

Shellac and carnauba wax are often used commercially to coat apples and citrus to improve appearance by adding gloss, to prevent water loss that leads to shriveling and subsequent loss of marketability, and to maintain quality through delayed ripening and senescence. Unfortunately, both materials are associated with non-food uses, and shellac has problems with low gas permeability that, although it leads to delayed ripening in some fruit (Baldwin et al., 1999), can also cause anaerobic conditions. Shellac also has problems with whitening, or “blushing” as it is referred to in the industry, when water condenses on the coated fruit surface after removal from cold storage. Nevertheless, shellac is recognized as one of the most shiny coatings, was found to improve the appearance and, it is assumed, increased subsequent sales of red and green apple cultivars such as ‘Delicious’ and ‘Granny Smith’, respectively (Bai et al., *in press*).

Carnauba wax is a natural plant wax with generally recognized as safe (GRAS) status (FDA, 1999), is relatively permeable to gases and, in microemulsion form, is quite shiny. The problem with carnauba wax is loss of gloss over storage time, and due to its relatively high gas permeability, it does not effectively delay ripening (Baldwin et al., 1999). However, it is an excellent barrier to water vapor, and can be combined with shellac to create a coating of moderate permeability to gases and low permeability to water vapor. However, the apple industry is concerned that consumers may object to shellac, which does not currently have GRAS status.

Zein is a natural protein found in corn kernels. Zein coatings have been used to coat nuts and candy for increased gloss, and prevention of oxidation and development of off-odors (Cosler, 1958). Extracting a zein–lipid mixture from ground corn costs only 2–4 US dollars per kg (Anon., 2001), and is a GRAS substance (FDA, 1999). Zein coatings offer a reasonable alternative to shellac and carnauba wax.

Surface coatings can decrease fruit peel permeance, modify the internal atmosphere, reduce water loss, and depress fruit respiration rate (Bai et

al., 2002; Banks et al., 1993; Hagenmaier and Shaw, 1992). Apple anatomy differs by cultivar in the number of stomates and lenticels which affects how the fruit react to surface coatings (Bai et al., *in press*). Therefore, selecting coatings with proper gas permeance for a particular cultivar is important (Bai et al., *in press*). Preliminary research showed that zein coatings with different zein and propylene glycol (PG) contents resulted in a wide range of internal CO<sub>2</sub> and O<sub>2</sub> partial pressures in coated apple fruit. It will benefit the fruit industry if alternative coatings to shellac and carnauba wax, with a wide range of gas permeabilities, were available to suit cultivar and/or commodity requirements.

Like shellac, zein also has whitening problems when in contact with water. Preliminary experiments showed that the whitening of zein-coated fruit was dependent on coating zein and PG contents.

In this work, an experimental zein coating series was formulated with different zein and PG contents. Permeability of coatings, internal atmosphere, gloss, and surface whitening were determined when the formulations were applied to various surfaces or to apple fruit. Finally, the overall effect of an optimal zein formulation on ‘Gala’ apple quality was investigated in comparison to commercial shellac- and carnauba wax-coated fruit.

## 2. Materials and methods

Zein was obtained from Sigma Chemical Co. (St. Louis, MO), and defatted by washing with hexane. The solvent used to dissolve the zein was 35% ethanol plus 35% isopropanol–water solution (by volume: 36.8 ml of 95% ethanol, 35 ml of 100% isopropanol, and 28.2 ml of water), except when described otherwise. This aqueous alcohol combination had been determined in preliminary work to be optimum for zein coating performance. PG was added as a plasticizer after testing of different plasticizers showed that only PG resulted in glossy zein-based coatings. A series of 4–15% zein combined with 2–16% PG coating formulations (4–15 g zein and 2–16 g PG to 94–69 g aqueous

alcohol) was generated for evaluating gas permeance and gloss characteristics when applied to apples.

To determine coating permeability, a polyethylene film was used as a carrier. Approximately 1 ml of each coating solution was deposited on the carrier film and was spread to a smooth level with a flexible blade. The film was dried for 2–4 weeks at 50% RH and 23 °C. Film thickness was measured using a caliper micrometer (Federal Products Co., Model XLI 20000, Providence, RI) taking measurements at six locations on the film and averaging the result. Thickness of the films ranged from 8 to 40 µm depending on the zein and PG concentration. O<sub>2</sub> and CO<sub>2</sub> permeance of the coated and uncoated polyethylene was determined at 30 °C and 60% RH with an oxygen analyzer (Ox-Tran 100, Modern Controls, Minneapolis, MN) and gas chromatograph (HP 5890A, Hewlett-Packard, Avondale, PA), respectively. The gas chromatograph was equipped with a CTR-1 column (1.8 m × 3.2 mm) packed with a porous polymer mixture connected to a thermal conductivity detector. Permeability was calculated by dividing the O<sub>2</sub> or CO<sub>2</sub> transmission rate by the gas partial pressure and multiplying by the film thickness (Hagenmaier and Shaw, 1991, 1992). Three to four replicates were made per formulation.

Coating shine in gloss units (GU) was measured with a reflectance meter (micro-TRI-gloss, BYK Gardner, Inc., Silver Spring, MD). Coatings were spread on polished test sheets (Leneta Co., Mahwah, NJ) at a thickness of 0.05 mm with a coating applicator (BYK-Gardner, Columbia, MD). Coated sheets were dried at 25 °C for 12 h after which reflectance was measured at an angle of 20°. Two test sheets were coated per formulation and 10 measurements made for each sheet.

Apples were obtained from Washington State. Non-coated, post-commercial controlled atmosphere stored ‘Gala’ and ‘Delicious’ apples were obtained from 1999 to 2001 from a commercial packinghouse, and sent to Winter Haven, FL, in a refrigerated truck.

Uniform defect-free fruit, weighing 180–200 g for ‘Gala’ and 200–245 g for ‘Delicious’ apples were equilibrated at room temperature (25 °C) for

24 h, prior to application of coatings. A formulation, “zein10”, with 10% zein plus 10% PG was used for comparison with two commercial coatings (EcoScience, Orlando, FL): Natural Shine TM 8000 (carnauba wax) and Apple Wax 55 (shellac) as well as with non-coated fruits as control. Coatings were applied using latex gloved hands at 0.5 ml per fruit (Bai et al., 2002). A pilot-plant scale conveyor dryer (Central Florida Sales and Service, Inc., Auburndale, FL) was used to dry fruit (including controls) at 50 °C for 5 min. Fruit were held at 20 °C and 50% RH. For non-coated controls, water was used instead of coating.

Coating gloss on the fruit surface of 4–5 fruit per treatment was measured with a reflectance meter. The reflectance meter was fitted with a shield having a 19 mm diameter hole (Hagenmaier and Baker, 1994), and reflectance was measured at an angle of 60°. Ten measurements were made per fruit.

Coated fruit surface whitening was measured by incubating the fruit at 50 °C, with at least 98% RH for 30 min, after which the fruit were moved to ambient conditions (20 °C, 50% RH) for 30 min and degree of whitening was measured. A whitening scale was developed and scored depending on relative area of discoloration with 5 = 70+% of the surface area discolored; 4 = 50–70%; 3 = 10–50%; 2 = 5–10%; 1 = 5% isolated spots; and 0 = none.

Flesh firmness was assessed with a penetrometer (FT 327, McCormick, Facchini, Alfonsine, Italy), equipped with a 1.1 cm diameter cylindrical plunger.

Samples for internal gas were obtained from the core cavity of fruit submerged in tap water (Alleyn and Hagenmaier, 2000). O<sub>2</sub> and CO<sub>2</sub> partial pressures were determined using a HP 5890A gas chromatograph equipped with a CTR-1 column (Alltech Associates, Deerfield, IL) consisting of an outer column (1.8 m × 6.4 mm) packed with activated molecular sieve and an inner column (1.8 m × 3.2 mm) packed with a porous polymer mixture connected to a thermal conductivity detector. O<sub>2</sub> partial pressure of samples was not corrected for argon, which is 0.9 kPa in air. Ethylene was measured with a PE 8500 gas chromatograph (Perkin-Elmer, Norwalk, CT)

equipped with an activated alumina column and a flame ionization detector (Baldwin et al., 1995). Ten individual fruit were used for each gas measurement. For weight loss determinations, 20 fruit were individually weighed initially and at the end of the storage period.

Analysis of sugars was accomplished using an HPLC system (Perkin–Elmer Series 410, Norwalk, CT) which separated sucrose, glucose, and fructose for quantification (Baldwin et al., 1991; Bett et al., 2000). Fruit homogenate with equivalent water (by volume) was kept at  $-20\text{ }^{\circ}\text{C}$  prior to analysis. Thawed homogenate was added to 80% ethanol, blended for 30 min, and vacuum-filtered through Whatman No. 4 filter paper. The resulting extract was passed through a C-18 Sep Pak (Waters/Millipore, Milford, MA) and a  $0.45\text{ }\mu\text{m}$  millipore filter. Filtered extract was analyzed using a Waters Sugar Pak column at  $90\text{ }^{\circ}\text{C}$ , with a mobile phase of  $100\text{ }\mu\text{M}$  ethylenediamine tetraacetic acid disodium-calcium salt (Ca EDTA), using a flow rate of  $0.5\text{ ml min}^{-1}$ , and a refractive index detector (Model LC-50, Perkin–Elmer, Norwalk, CT).

For titratable acidity (TA) analysis, homogenates were centrifuged at  $25,000\times g$  and the supernatant titrated to pH 8.1 with  $0.1\text{ N}$  NaOH, and the acidity was calculated as malic acid on weight basis (gram per kilogram) (Jones and Scott, 1984).

For volatile analysis (Bai et al., 2002), 50 g apple slices (core tissue removed) were homogenized with 25 ml deionized water and 25 ml saturated NaCl solution. Two milliliters of homogenate were then placed into a 6 ml vial sealed with a crimp-top and Teflon–silicone septum, flash-frozen in liquid nitrogen and stored at  $-80\text{ }^{\circ}\text{C}$  prior to analysis. Sample vials were thawed under running tap water, heated rapidly to  $80\text{ }^{\circ}\text{C}$ , and incubated for 15 min by a Perkin–Elmer HS-6 headspace sampler heating block before headspace was pressurized and injected onto the GC column. Analysis was carried out using a gas chromatograph (Perkin–Elmer Model 8500, Norwalk, CT) equipped with a  $0.53\text{ mm}\times 30\text{ m}$  polar Stabilwax capillary column ( $1.0\text{ }\mu\text{m}$  film thickness, Restek, Bellefonte, PA) and a flame ionization detector. Oven temperature was held at  $40\text{ }^{\circ}\text{C}$  for 6 min,

then raised to  $180\text{ }^{\circ}\text{C}$  at a rate of  $6\text{ }^{\circ}\text{C min}^{-1}$ . Compounds were identified by comparison of retention times with those of standards and by enrichment of apple homogenate with authentic samples. Concentrations were calculated by using regression equations determined by injecting five different concentrations of each standard to obtain a peak height calibration curve as described by Nisperos-Carriedo et al. (1990). Identification of volatiles was periodically checked by spiking homogenate with standards. Volatile components that are abundant, or that have been reported to have significance for apple or other fruit flavors (Mattheis et al., 1995) were analyzed including ethanol, ethyl acetate, ethyl butyrate, butyl acetate, 2-methylbutyl acetate and hexyl acetate.

Sensory panel analyses for sweetness, acidity, texture, off-flavor and flavor were conducted by 20 experienced panelists using hedonic scales. Quality factors were scored on a 9-point scale with 9 = high intensity or very firm to 1 = low intensity or soft.

PROC GLM of SAS Version 6.12 (SAS Institute, Cary, NC) was used for analysis of variance. Mean separation was determined by the Scheffe's test.

### 3. Results and discussion

#### 3.1. Solubility of zein

Zein is soluble in aqueous alcohol. To formulate a 10% zein solution, the alcohol:water (v/v) had to be 6:4 to 9:1. Aqueous alcohol solutions with either ethanol, isopropanol, or their mixture were equally effective as a zein solvent, and did not affect coating gloss (data not shown). Viscosity increased with increased zein content, with a 15% zein formulation being the limit for commercial coating use. Insolubility of zein in water is due to its amino acid composition (Reiners et al., 1973). The advantage of using an alcohol solvent is the reduction of drying time, but the shortcomings are increased coating cost and an increase in volatile organic compounds (VOCs) which can become a regulatory issue. A commercial water-soluble zein is sold by Freeman Industries, L.L.C (Tuckahoe,

NY) but the gloss and other coating properties are not compatible for coating apple fruits.

### 3.2. Gloss

Combinations of zein and PG contents in the aqueous alcohol solutions affected the gloss of coatings. PG was added as a plasticizer, without which zein coatings are very brittle. PG (2%) combined with any amount of zein did not result in gloss differences on ‘Gala’ apples compared with control. Gloss increased only when PG concentrations were increased from 2 to 6%, after which increasing PG did not result in significant increases in gloss (Fig. 1). However, gloss increased along with increasing zein content up to 15% zein (Fig. 1, Table 1), above which viscosity became a problem.

Gloss of non-coated ‘Gala’ was 7.3 GU, which was higher than that of ‘Delicious’ which was 4.1 GU. To the human eye, ‘Gala’ apples appear to have a natural gloss, but ‘Delicious’ fruit have very low gloss. This is one reason that has led the apple industry, generally, to apply a shiny coating to red ‘Delicious’ apples. When formulating zein coatings, alteration of zein and/or PG content resulted in a wide range of gloss options. Mixtures of less than 10% zein and 4% PG resulted in coatings of

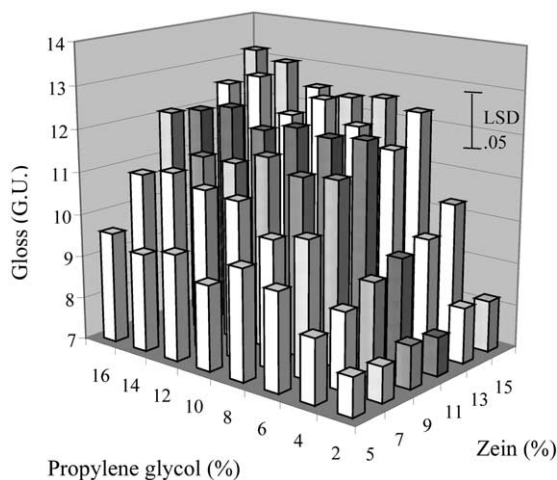


Fig. 1. Effect of zein and PG contents on gloss of ‘Gala’ apple. Non-coated control was 7.3 GU ( $n = 100$ ).

Table 1

Gloss of zein coatings on test sheets and on ‘Delicious’ apple

Combination (wt.%)		Gloss (GU)	
Zein	PG	Test sheet <sup>a</sup>	‘Delicious’ apple <sup>b</sup>
15	15	16.5 a <sup>c</sup>	11.2 a
15	4	3.3 e	–
12	8	10.2 c	7.8 b
10	8	9.1 c	6.9 bc
10	4	2.8 e	5.6 d
8	15	12.1 b	6.8 bc
8	8	8.7 cd	6.3 c
4	15	8.5 d	4.4 d
4	4	2.3 e	–
0	0	2.4 e	4.1 d

<sup>a</sup> Three test sheets were coated at a thickness of 0.05 mm and incubated at 20 °C overnight and then 10 measurements for each sheet were made at an angle of 20°.

<sup>b</sup> Five fruit were coated and stored at 20 °C for 2 days and then 10 measurements for each fruit were made at an angle of 60°. The fruit were stored in CA for 6 months before being used.

<sup>c</sup> Mean values ( $n = 30$  for sheet and  $n = 50$  for apple) in same column that are not followed by the same letter are significantly different ( $P < 0.05$ ).

low gloss that would not be commercially acceptable to the apple industry, but might be useful for other types of fruit where a more natural appearance is preferred.

### 3.3. Whitening

Zein content was the key factor for whitening of zein-coated fruit. When zein content was higher than 11%, the degree of whitening was rated higher than 1.3, indicating that, most of the fruit exhibited white spots (scale of 1), and quite a number of them exhibited whitening on over 5–10% of the fruit surface area (Fig. 2). The discolored area increased with increasing zein content. Lower than 4% PG in coating formulations further increased whitening. Therefore, the combination with less than 11% zein and more than 4% PG is desirable for minimal discoloration.

Whitening on shellac-coated apples has been recognized (Baldwin, 1994). Whitening spots on ‘Delicious’ apples were exhibited when the shellac content was higher than 4%, and the degree of



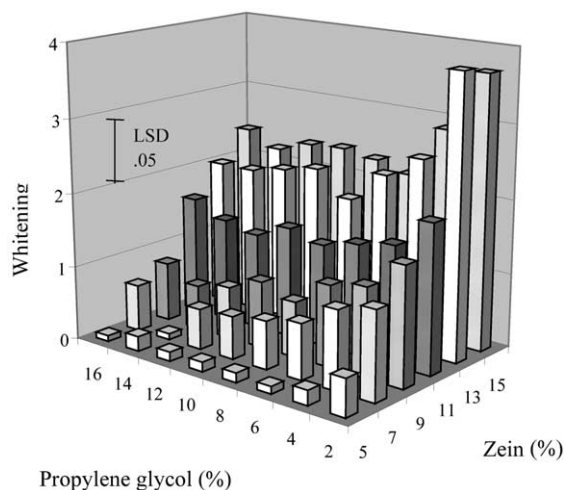


Fig. 2. Effect of zein and PG contents in coatings on whitening of 'Gala' apple ( $n = 10$ ).

whitening was increased by increasing shellac contents in a carnauba-shellac emulsion coating with a 20% total solids (unpublished data). A starch-based coating (Bai et al., 2002) also showed whitening when coated on 'Delicious' apple (unpublished data). However, no whitening occurred on carnauba- and candelilla waxes-coated apples. This indicates that whitening can be somewhat controlled by regulating type and ratio of material in the coating formulation, ingredients, and the content.

### 3.4. Permeability and internal gas

Average permeability of zein coatings was  $5.4 \times 10^{-16} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$  for  $\text{CO}_2$  and  $1.2 \times 10^{-16} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$  for  $\text{O}_2$  (Table 2). Zein and PG contents had little effect on gas permeability. In comparison, a typical shellac coating had  $1.4 \times 10^{-16} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$  for  $\text{CO}_2$  and  $0.4 \times 10^{-16} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$  for  $\text{O}_2$ , while a more permeable carnauba-shellac mixture had  $12.1 \times 10^{-16} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$  for  $\text{CO}_2$  and  $2.6 \times 10^{-16} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$  for  $\text{O}_2$ .

Coatings with low permeability offer more of a barrier to gas exchange between the fruit internal atmosphere and the external atmosphere, resulting in a modified internal fruit atmosphere of relatively high  $\text{CO}_2$  and low  $\text{O}_2$ . This can benefit fruit shelf life in the same way that controlled atmosphere or modified atmosphere packaging does. Appropriate internal low  $\text{O}_2$  and high  $\text{CO}_2$  partial pressures can lower respiration rate, maintain flesh firmness, and retard ripening and senescence (Bai et al., 2002; Banks et al., 1993). Less modification of the internal fruit atmosphere gives less benefit in terms of ripening control, while excessive modification can cause anaerobic metabolism (Ueda et al., 1993; Yearsley et al., 1996).

Contents of zein and PG in coatings affected internal  $\text{CO}_2$  and  $\text{O}_2$  partial pressures. Generally, the zein content correlated with gas modification

Table 2  
 $\text{CO}_2$  and  $\text{O}_2$  permeability of zein and other coatings at 20 °C and 60% RH

Combination (wt.%)		Permeability ( $10^{-16} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ )		$\text{CO}_2/\text{O}_2$
Zein	PG	$\text{CO}_2$	$\text{O}_2$	
15	15	4.1 c <sup>a</sup>	0.8 c	5.4
15	4	5.4 c	1.4 b	3.9
8	15	4.3 c	1.7 b	2.5
8	8	4.9 c	0.9 bc	5.1
4	15	3.6 c	1.0 bc	3.3
4	4	9.8 b	1.3 bc	7.5
Average of zein coatings		5.4	1.2	4.6
Shellac		1.4 d	0.4 d	4.5
Carnauba-shellac		12.1 a	2.6 a	4.6

<sup>a</sup> Mean values ( $n = 3$  or 4) in same column that are not followed by the same letter are significantly different ( $P < 0.05$ ).

Table 3

Internal gases and weight loss of ‘Gala’ apples coated with different zein and PG combinations and stored at 20 °C for 14 days

Combination (wt.%)		Internal gases (kPa)		$\Delta P_{\text{CO}_2}/\Delta P_{\text{O}_2}$ <sup>a</sup>	Weight loss (%)
Zein	PG	CO <sub>2</sub>	O <sub>2</sub>		
15	15	11.0 a <sup>b</sup>	6.0 a	0.73 d	1.7 a
15	8	11.4 a	5.6 a	0.74 d	1.7 a
15	4	9.4 a	10.2 b	0.87 c	1.9 a
8	15	4.9 b	17.6 c	1.46 b	2.4 b
8	8	4.3 b	18.3 c	1.59 b	2.6 b
8	4	4.5 b	18.2 c	1.61 b	2.6 b
4	15	4.0 bc	18.5 cd	1.66 b	2.5 b
4	8	3.9 bc	18.7 cd	1.69 b	2.6 b
4	4	3.6 c	18.9 cd	1.75 b	2.8 b
0	0	1.7 d	20.6 d	4.44 a	4.4 c

Fruit had been previously stored in CA for 3 months before being used.

<sup>a</sup>  $\Delta P_{\text{CO}_2}$  and  $\Delta P_{\text{O}_2}$ : CO<sub>2</sub> and O<sub>2</sub> partial pressure differences across the peel, respectively.<sup>b</sup> Mean values ( $n = 10$ ) in same column that are not followed by the same letter are significantly different ( $P < 0.05$ ).

in the fruit (Table 3). Gas exchange between internal fruit and external atmosphere is by permeation through cuticle and by diffusion through pores (Banks et al., 1993). Application of surface coatings covers the cuticle and may plug pores on the fruit surface (Banks, 1984; Banks et al., 1993; Ben-Yehoshua et al., 1985) depending on viscosity, surface tension, and other factors. Ratios of permeabilities between CO<sub>2</sub> and O<sub>2</sub> (Table 2) were 2.5–7.5 for coatings, and the ratio of diffusion through air between them was reported to be 0.78 at 0 °C (Weast, 1988). If the dominant pathway for gas exchange is by permeation through the peel (i.e. through a barrier), the ratio of pressure differences across the peel ( $\Delta P_{\text{CO}_2}/\Delta P_{\text{O}_2}$ ) is expected to be smaller than if pore diffusion (i.e. through air) is the dominant pathway (Bai et al., in press). Since the relation between zein content and  $\Delta P_{\text{CO}_2}/\Delta P_{\text{O}_2}$  was negatively correlated, it can be inferred that the higher zein content tended to result in more blocked pores. Uncoated fruit, for example, had the highest pressure difference value ( $\Delta P_{\text{CO}_2}/\Delta P_{\text{O}_2}$ ) of 4.44 while coatings with 15% zein had values less than 1.0 (Table 3). The total partial pressures of O<sub>2</sub> and CO<sub>2</sub> were roughly 21–22 kPa for zein contents of 8% and less, which also indicates diffusion through pores (Table 3). PG content in

most formulations generally did not affect fruit internal gas partial pressures, except when zein was 15% and PG content was 4–8%. These formulations led to changes in internal O<sub>2</sub> partial pressures (Table 3). When PG content was 8–15%, the coating tended to block pores in the peel; thus, the gas exchange between internal and external atmosphere was more dependent on permeance than diffusion. In contrast, when PG was 4%, the gas exchange through the pores in the peel increased. Banks et al. (1993) reported that coatings mainly exert their effects on peel resistance to diffusion of gases by blocking a greater or lesser proportion of the pores on the fruit surface. When the PG level was 4%, the resulting coating blocked the pores less than when PG levels in the formulations were higher.

Retardation of water loss is another benefit derived from application of coatings to fruit. Weight loss of ‘Gala’ apple reached 4.4% at 20 °C in the non-coated control (Table 3). Shrinkage was observed (shriveling of the peel), and the fruit were less firm to the touch than they had been at the start of the experiment. Zein coatings kept the weight loss to less than 2.8%, with the 15% zein coating resulting in fruit with weight loss less than 1.9%. No shrinkage was detected for zein-coated fruit. Hatfield and Knee (1988) and Maguire et al.

(2000) reported that even as little as 3.5–5% weight loss can lead to shrivel in apples.

### 3.5. Quality of zein-coated fruit

Based on previous experiments, an optimal coating of 10% zein and 10% PG (zein10) was used for investigating the effect of zein coating on ‘Gala’ apple quality compared with commercial shellac, carnauba, and a non-coated control. Zein10-coated fruit exhibited modified internal O<sub>2</sub> and CO<sub>2</sub> partial pressures between that found for carnauba- and shellac-coated fruit (Table 4) with 10.6 kPa CO<sub>2</sub>+8.2 kPa O<sub>2</sub>. The zein coating

induced a 17-fold increase in ethanol content compared with non-coated control. Shellac modified the internal fruit atmosphere such that shellac-coated apples had the highest and lowest CO<sub>2</sub> and O<sub>2</sub> partial pressures, respectively, and had a similar ethanol content to that of zein-coated fruit. Carnauba wax-coated apples exhibited the least difference in internal atmosphere compared with non-coated controls with no significant increase in ethanol. Zein10 and shellac coatings also resulted in increased butyl acetate and 3-methylbutyl-2-methylbutyrate concentrations, which are reported to have apple-like or fruit-like aromas. Zein10-coated fruit were rated

Table 4

Effect of coating on internal gases, weight loss, sugar, acidity, volatiles, and sensory quality of ‘Gala’ apples stored at 21 °C for 14 days

	N <sup>a</sup>	Control	Carnauba	Zein10	Shellac
Gloss	100	5.2 c <sup>b</sup>	7.2 b	8.9 ab	9.5 a
Whitening	10	0 c	0 c	0.9 b	2.6 a
Internal gases (kPa)	10				
CO <sub>2</sub>		2.6 d	8.8 c	10.6 b	12.3 a
O <sub>2</sub>		18.3 a	10.1 b	8.2 c	6.1 d
Weight loss (%)	20	3.0 a	1.8 d	2.3 b	2.0 c
Firmness (N)	20	66 ab	61 b	63 b	73 a
Sugar (g kg <sup>-1</sup> )	4				
Sucrose		0.30 a	0.32 a	0.31 a	0.30 a
Glucose		0.22 a	0.20 a	0.21 a	0.22 a
Fructose		0.68 a	0.63 b	0.68 a	0.67 a
pH	4	4.1 a	4.0 a	4.0 a	4.1 a
Titrateable acidity (g kg <sup>-1</sup> )	4	2.5 a	2.7 a	2.8 a	2.9 a
Volatiles (μg kg <sup>-1</sup> )	4				
Ethanol		1.12 b	1.94 b	18.21 a	18.76 a
Ethyl acetate		0.05 a	0.03 a	0.03 a	0.05 a
Ethyl propionate		0.01 b	0.03 b	0.11 a	0.12 a
Butyl acetate		0.25 ab	0.22 b	0.29 a	0.28 a
3-Methylbutyl-2-methylbutyrate		0.07 b	0.06 b	0.12 a	0.12 a
Sensory test	20				
Sweetness		6.1 a	5.2 b	5.7 a	5.9 a
Acidity		3.7 b	4.4 a	4.2 a	4.2 a
Texture		5.7 a	5.9 a	6.4 a	6.6 a
Off-flavor		2.6 b	4.1 a	2.4 b	3.0 b
Flavor		6.1 a	5.5 b	6.5 a	5.8 ab

Fruit had been previously stored in CA for months before being used.

<sup>a</sup> Replicate number.

<sup>b</sup> Mean values in same row that are not followed by the same letter are significantly different ( $P < 0.10$  for sensory test (Meilgaard et al., 1991) and  $P < 0.05$  for others).



highest for flavor and lowest for off-flavor in a sensory test. Carnauba-coated fruit had lower levels of the above volatiles compared with zein10- or shellac-coated fruit and scored lowest for flavor and highest for off-flavor in the sensory test. Results indicate that the increase in ethanol levels in zein10-coated fruit did not impair apple flavor, when other important flavor esters were simultaneously increased (Table 4).

The major sugar in ‘Gala’ apples was fructose which was 0.63–0.68 g kg<sup>-1</sup> (fresh weight basis), and then sucrose and glucose with contents of 0.30–0.32 and 2.0–2.2 g kg<sup>-1</sup>, respectively, in non-coated control fruit. Coated fruit had similar sugar levels and no differences were found due to treatment except for lower fructose levels in carnauba-coated fruit, which was confirmed in the sensory panelists’ ratings for sweetness (Table 4).

Juice pH of ‘Gala’ was 4.0–4.1, and TA was 2.5–2.9 g kg<sup>-1</sup> (fresh weight basis, Table 4). No difference was apparent in pH or TA. Coated apples tended to have lower pH and higher TA than non-coated controls, but the differences in acidity ratings by the sensory panel were significant, with coated fruit being rated higher in acid flavor than controls.

Shellac-coated fruit exhibited the highest flesh firmness as determined by the penetrometer (Table 4), most likely due to delayed ripening caused by a modification of the internal atmosphere or due to less weight (water) loss. However, there were no significant differences for firmness in the sensory test. Since control fruit lost more water than coated fruit, causing shrinkage (Table 3), this may have falsely elevated the sensory response to firmness (Table 4).

In summary, an optimum zein formulation was developed that provided shine, resulted in a desirable modified atmosphere, and exhibited minimal whitening when applied to apple fruit under simulated commercial conditions. Zein10 coating maintained apple quality similar to a commercial shellac formulation, and extended apple shelf life compared with non-coated controls or commercial carnauba wax-coated fruit.

## Acknowledgements

Funding for this research was provided by a grant from the Washington Tree Fruit Research Commission.

## References

- Alleyne, V., Hagenmaier, R.D., 2000. Candelilla–shellac—an alternative formulation for coating apples (*Malus domestica* Borkh). *HortScience* 35, 691–693.
- Anon., 2001. Corn extract for waxing paper. *Agric. Res.* (3), 23.
- Bai, J., Baldwin, E.A., Hagenmaier, R.D., 2002. Alternatives to shellac coatings provide comparable benefits in terms of gloss, internal gases modification, and quality of ‘Delicious’ apple fruit. *HortScience* 37, 559–563.
- Bai, J., Baldwin, E.A., Hagenmaier, R.D., in press. Coating selection for apples other than ‘Delicious’. *Postharvest Biol. Technol.*
- Baldwin, E.A., 1994. Edible coatings for fresh fruits and vegetables: past, present, and future. In: Krochta, J.M., Baldwin, E.A., Nisperos-Carriedo, M.O. (Eds.), *Edible Coatings and Films to Improve Food Quality*. Technomic Publishing Co, Lancaster, PA, pp. 25–64.
- Baldwin, E.A., Nisperos-Carriedo, M.O., Moshonas, M.G., 1991. Quantitative analysis of flavor and other volatiles for certain constituents of two tomato cultivars during ripening. *J. Am. Soc. Hort. Sci.* 116, 265–269.
- Baldwin, E.A., Nisperos, M.O., Shaw, P.E., Burns, J.K., 1995. Effect of coatings and prolonged storage conditions on fresh orange flavor volatiles, degrees brix, and ascorbic acid levels. *J. Agric. Food Chem.* 43, 1321–1331.
- Baldwin, E.A., Burns, J.K., Kazokas, W., Brecht, J.K., Hagenmaier, R.H., Bender, R.J., Pesis, E., 1999. Effect of two edible coatings with different permeability characteristics on mango (*Mangifera indica* L.) ripening during storage. *Postharvest Biol. Technol.* 17, 215–226.
- Banks, N.H., 1984. Studies of the banana fruit surface in relation to the effects to TAL prolong coating on gaseous exchange. *Sci. Hort.* 24, 279–286.
- Banks, N.H., Dadzie, B.K., Cleland, D.J., 1993. Reducing gas exchange of fruits with surface coatings. *Postharvest Biol. Technol.* 3, 269–284.
- Ben-Yehoshua, S., Burg, S.P., Young, P., 1985. Resistance of citrus fruit to mass transport of water vapor and other gases. *Plant Physiol.* 79, 1048–1053.
- Bett, K.L., Ingram, D.A., Grimm, C.C., Lloyd, S.W., Spanier, A.M., Miller, J.M., Gross, K.C., Baldwin, E.A., Vinyard, B.T., 2000. Flavor of fresh-cut Gala apples in barrier film packaging as affected by storage time. *J. Food Qual.* 24, 141–156.
- Cosler, H.B., 1958. Prevention of staleness, rancidity in nut meats and peanuts. *Peanut J. Nut World* 37, 10–11, 15.

- FDA, 1999. Code of Federal Regulations (CFR). Food and Drug Administration, US Government Printing Office, Washington, DC.
- Hagenmaier, R.D., Baker, R.A., 1994. Internal gases, ethanol content and gloss of citrus fruit coated with polyethylene wax, carnauba wax, shellac or resin at different application levels. *Proc. Fla. State Hort. Soc.* 107, 261–265.
- Hagenmaier, R.D., Shaw, P.E., 1991. The permeability of shellac coatings to water vapor and other gases. *J. Agric. Food Chem.* 39, 825–829.
- Hagenmaier, R.D., Shaw, P.E., 1992. Gas permeability of fruit coating waxes. *J. Am. Soc. Hort. Sci.* 117, 105–109.
- Hatfield, S.G.S., Knee, M., 1988. Effects of water loss on apple in storage. *Int. J. Food Sci. Technol.* 23, 575–583.
- Jones, R.A., Scott, S.L., 1984. Genetic potential to improve tomato flavor in commercial F1 hybrids. *J. Am. Soc. Hort. Sci.* 109, 318–321.
- Maguire, K.M., Banks, N.H., Alexander, L., Gardon, I.L., 2000. Harvest date, cultivar, orchard, and tree effects on water vapor permeance in apples. *J. Am. Soc. Hort. Sci.* 125, 100–104.
- Mattheis, J.P., Buchanan, D.A., Fellman, J.K., 1995. Volatile compound production by Bisbee Delicious apples after sequential atmosphere storage. *J. Agric. Food Chem.* 43, 194–199.
- Meilgaard, M., Civille, G.V., Carr, B.T., 1991. *Sensory Evaluation Techniques*, 2nd ed.. CRC Press, Boca Raton, FL.
- Nisperos-Carriedo, M.O., Shaw, P.E., Baldwin, E.A., 1990. Changes in volatile flavor components in 'Pineapple' orange juice as influenced by the application of lipid and composite films. *J. Agric. Food Chem.* 38, 1382–1387.
- Reiners, R.A., Wall, J.S., Inglett, G.E., 1973. Corn proteins: potential for their industrial use. In: Pomeranz, Y. (Ed.), *Industrial Uses of Cereals*. American Assn. of Cereal Chemists, Inc, St. Paul, MN, p. 285.
- Ueda, Y., Bai, J., Yoshioka, H., 1993. Effects of polyethylene packaging on flavor retention and volatile production of Starking Delicious apple. *J. Jpn. Soc. Hort. Sci.* 62, 207–213.
- Weast, R.C., 1988. *CRC Handbook of Chemistry and Physics*, 69th ed.. CRC Press, Boca Raton, FL, p. F48.
- Yearsley, C.W., Banks, N.H., Ganesh, S., Cleland, D.J., 1996. Determination of lower oxygen limits for apple fruit. *Postharvest Biol. Technol.* 8, 95–109.